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13. ABSTRACT (Maximum 200 words) The lithium arsenides {Li ₂ [μ ₂ -As(SiMe ₃) ₂][μ ₃ -As(SiMe ₃) ₂](THF)] ₂ (I) (THF = tetrahydrofuran) and [(Me ₃ Si) ₂ AsLi(THF) ₂] ₂ (II) were isolated and their solid-state structures determined by X-ray methods. Compound I crystallizes in the monoclinic system, space group <i>P</i> 2 ₁ / <i>c</i> , with <i>a</i> = 10.147(1) Å, <i>b</i> = 19.665(2) Å, <i>c</i> = 16.768(2) Å, β = 107.78(1)° and <i>Z</i> = 2. The core structure consists of an [LiAs] ₄ ladder-like framework with four antiparallel adjacent As-Li rungs. The two lithium atoms of the central ring each bridge three arsenic centers while the two lithium atoms belonging solely to the outer rings each span two arsenic atoms and are coordinated to one THF molecule. Monoclinic crystals of compound II belong to space group <i>C</i> 2/ <i>c</i> , with <i>a</i> = 17.877(4) Å, <i>b</i> = 14.077(3) Å, <i>c</i> = 19.006(4) Å, β = 109.16(2)° and <i>Z</i> = 4. The structure consists of a centrosymmetric dimer containing a four-membered As-Li-As-Li ring wherein each lithium atom is coordinated to two molecules of THF.					
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**ISOLATION AND X-RAY CRYSTAL STRUCTURES OF
[Li[μ_2 -As(SiMe₃)₂][μ_3 -As(SiMe₃)₂](THF)]₂ and [(Me₃Si)₂AsLi(THF)₂]₂**

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Isolation and X-ray Crystal Structures of $\{\text{Li}_2[\mu_2\text{-As}(\text{SiMe}_3)_2][\mu_3\text{-As}(\text{SiMe}_3)_2](\text{THF})\}_2$ and $[(\text{Me}_3\text{Si})_2\text{AsLi}(\text{THF})_2]_2$

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The lithium arsenides $\{\text{Li}_2[\mu_2\text{-As}(\text{SiMe}_3)_2][\mu_3\text{-As}(\text{SiMe}_3)_2](\text{THF})\}_2$ (I) (THF = tetrahydrofuran) and $[(\text{Me}_3\text{Si})_2\text{AsLi}(\text{THF})_2]_2$ (II) were isolated and their solid-state structures determined by X-ray methods. Compound I crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 10.147(1) \text{ \AA}$, $b = 19.665(2) \text{ \AA}$, $c = 16.768(2) \text{ \AA}$, $\beta = 107.78(1)^\circ$ and $Z = 2$. The core structure consists of an $[\text{LiAs}]_4$ ladder-like framework with four antiparallel adjacent As-Li rungs. The two lithium atoms of the central ring each bridge three arsenic centers while the two lithium atoms belonging solely to the outer rings each span two arsenic atoms and are coordinated to one THF molecule. Monoclinic crystals of compound II belong to space group $C2/c$, with $a = 17.877(4) \text{ \AA}$, $b = 14.077(3) \text{ \AA}$, $c = 19.006(4) \text{ \AA}$, $\beta = 109.16(2)^\circ$ and $Z = 4$. The structure consists of a centrosymmetric dimer containing a four-membered As-Li-As-Li ring wherein each lithium atom is coordinated to two molecules of THF.

KEYWORDS: Arsenide, lithium, crystal structure.

INTRODUCTION

Lithium compounds are among the most widely used organometallic reagents, yet their structure and bonding is far from trivial. The high degree of ionic character of lithium dominates its bonding and though the octet rule is not adequate for interpreting this bonding, the coordination geometry about lithium is often tetrahedral.¹ The degree of oligomerization or aggregation generally correlates with the reactivity of these reagents and the degree of association in solution is often reflected in the solid-state structure.² Predicting the structure of lithium compounds is difficult and appears to depend on the nature and size of electron-donating ligands as well as the steric size of neutral ligands. The presence of electron rich species can alter the aggregation of these complexes dramatically.

The isolation of $\{\text{Li}_2[\mu_2\text{-As}(\text{SiMe}_3)_2][\mu_3\text{-As}(\text{SiMe}_3)_2](\text{THF})\}_2$ (I) (THF = tetrahydrofuran) prompted attempts to crystallize two similar lithium arsenides, $[(\text{Me}_3\text{Si})_2\text{AsLi}(\text{THF})_2]_2$ (II) and solvent free $\text{LiAs}(\text{SiMe}_3)_2$. Although the crystal structures of the phosphorus analogues of these compounds have been determined,^{3,4} the arsenides could not be assumed to be isostructural. The structures of $[(\text{Et}_2\text{O})_2\text{LiAsPh}_2]_2$,⁵ $[(\text{Et}_2\text{O})\text{LiPPh}_2]_\infty$ ⁶ and $[(\text{THF})_2\text{LiPPh}_2]_\infty$ ⁶ have been reported and are obviously quite different. In addition, the solid-state structures of several lithium arsenides including $\{(\text{THF})\text{Li}[\text{As}(\text{tBu})\text{As}(\text{tBu})_2]\}_2$ ⁷ and $[(1,4\text{-dioxane})_3\text{LiAsPh}_2]$ ⁵ have been established by X-ray analyses but their related phosphorus analogues have yet to be prepared. Herein, the isolation and solid-state structures of I and II and the attempted isolation of crystalline $\text{LiAs}(\text{SiMe}_3)_2$ are presented.

EXPERIMENTAL

General considerations

All manipulations were performed by Schlenk techniques or in a Vacuum/Atmospheres HE-493 Dri-Lab under argon. THF, benzene and benzene- d_6 were distilled from sodium/benzophenone under dry nitrogen. Pentane was distilled from LiAlH_4 under dry nitrogen. Ether-free $\text{LiAs}(\text{SiMe}_3)_2$ was prepared by heating the THF solvated compound⁸ at 70 °C for 48 hours at 10^{-3}

torr. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained on a Varian XL-300 (300 and 75.4 MHz, respectively) spectrometer using 5 mm tubes. ^1H and ^{13}C spectra were referenced to TMS using the residual protons or carbons of deuterated benzene at δ 7.15 or 128 ppm. NMR tubes were flame sealed under vacuum. All melting points (uncorrected) were obtained with a Thomas-Hoover Uni-melt apparatus and capillaries were flame sealed under argon. Crystals used in the X-ray analyses were flame sealed in 0.7 mm glass capillaries. Elemental analysis was performed by E+R Microanalytical Laboratory, Inc., Corona, New York.

$\{\text{Li}_2[\mu_2\text{-As}(\text{SiMe}_3)_2][\mu_3\text{-As}(\text{SiMe}_3)_2](\text{THF})\}_2$ (I)

Three mole equivalents of ether-free $\text{LiAs}(\text{SiMe}_3)_2$ (0.300 g, 1.31 mmol) was added to a stirring benzene suspension of InCl_3 (0.969 g, 0.438 mmol). Several drops of THF were added to the vial in which the arsenide was weighed and the resulting solution was added to the InCl_3 suspension in order to assure a quantitative transfer. After addition of the THF portion, the solution immediately became dark as a brown/black precipitate formed. The solution was cannula filtered after it had been stirred for 24 hours at room temperature. The volatiles were removed from the orange filtrate in *vacuo*, leaving an orange viscous oil. A black powder that remained in the original flask was washed with pentane which was then added to the filtrate. The orange oil was dissolved in pentane and the solution was cooled to -15°C . After 1 week, colorless crystals of I suitable for an X-ray diffraction analysis had grown from this solution (0.007 g). Anal. Found for the black powder: As, 25.86; In, 40.13. ^1H NMR of crystals: δ 0.63 (s, SiMe_3), 1.18 (m, CH_2 of THF), 3.65 (bm, OCH_2 of THF). No signal was observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum due to the small sample size.

$[(\text{Me}_3\text{Si})_2\text{AsLi}(\text{THF})_2]_2$ (II)

To a pentane suspension of ether-free $\text{LiAs}(\text{SiMe}_3)_2$ was added enough THF to dissolve all of the solid. Large colorless crystal of II were grown by slow evaporation of the solution over a several day period. Upon decanting the supernatant, the crystals immediately began to turn white

on the surface and they ultimately flaked apart to a powder. *This powder immediately ignites upon introduction to air and may be explosive in less than 0.1 g quantities.* Crystal fragments of an appropriate size for X-ray analysis were sealed inside glass capillaries the interior walls of which had been previously moistened with a pentane/THF solution. mp: The crystals became opaque white from 54-60 °C and showed no further change up to 290 °C. Anal. Calcd. (Found) for $C_{24}H_{68}As_2Li_2O_4Si_4$: C, 45.15 (45.02); H, 9.2 (9.21); As, 20.12 (20.41); Li, 1.86 (1.67). 1H NMR: δ 0.62 (s, $SiMe_3$), 1.42 (m, CH_2 of THF), 3.72 (m, OCH_2 of THF). ^{13}C NMR: δ 8.13 (s, $SiMe_3$), 25.42 (s, CH_2 of THF), 68.61 (s, OCH_2 of THF).

Crystallographic data collection and structure determination

An Enraf-Nonius CAD-4 diffractometer (Cu- $K\alpha$ radiation; graphite monochromator) was used for all measurements on compounds **I** and **II**. Crystallographic data and summaries of the analyses are provided in Table 1. Refined unit-cell parameters were derived in each case from the diffractometer setting angles for 25 reflections ($30^\circ < \theta < 35^\circ$ for **I**, $36^\circ < \theta < 40^\circ$ for **II**) widely separated in reciprocal space. Intensity data were corrected for the usual Lorentz and polarization effects. Empirical absorption corrections, derived from the ϕ -dependency of the intensities of several reflections with ψ ca. 90° , were also applied. The space group $P2_1/c$ for **I** was established uniquely by the Laue symmetry and systematic absences ($0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$). For **II**, the systematic absences ($hk0$ when $h + k \neq 2n$, $h0l$ when $l \neq 2n$) are compatible with space groups Cc and $C2/c$; the latter was assumed at the outset and shown to be correct by the structure solution and refinement.

The crystal structure of **I** was solved by direct methods (MULTAN11/82). Approximate coordinates for the As and Si atoms were derived from an E -map. The other non-hydrogen atoms were located in a series of weighted F_o and difference Fourier syntheses phased successively by an increasing number of atoms. For **II**, coordinates for the isomorphous phosphorus analogue³ were used as input for the initial structure-factor calculation. Non-hydrogen atom positional and thermal parameters for **I** and **II** (at first isotropic and then anisotropic) were adjusted by means of

several rounds of full-matrix least-squares calculations. Hydrogen atoms were incorporated at their calculated positions during the later least-squares iterations; an extinction correction was also included as a variable for **II**. Parameter refinements converged at $R = 0.053$ ($R_w = 0.072$) for **I** and $R = 0.060$ ($R_w = 0.084$) for **II** over 1832 and 2463 reflections, respectively, with $I > 3.0\sigma$ (I). Final difference Fourier syntheses contained no unusual features.

Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP). For structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. 9.

RESULTS AND DISCUSSION

On reaction of ether-free $\text{LiAs}(\text{SiMe}_3)_2$ with InCl_3 in a 3:1 mole ratio in a benzene/THF solution, the anticipated products were a trisarsinoindane and lithium chloride. The formation of a black precipitate indicated that this reaction did not proceed as expected. A partial elemental analysis revealed that the composition of this material was 25.86% As and 40.13% In, i.e. a 1:1.01 mole ratio. Since all of the material was used for elemental analysis, its identity as InAs , a mixture containing elemental indium and arsenic or an organometallic compound could not be established. In addition to the black precipitate, a small number of colorless crystals were isolated. ^1H NMR spectroscopy and a single-crystal X-ray analysis identified these crystals as **I**. An ORTEP diagram showing the solid-state structure and atom numbering scheme is presented in Figure 1. Several of the methyl carbon atoms are extremely anisotropic; the magnitude and orientations of their thermal ellipsoids suggest crystal packing disorder. Table 2 lists the non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters. Selected interatomic distances and angles are given in Table 3.

Crystals of compound **I** are not isomorphous with those of the phosphorus analogue $\{\text{Li}_2[\mu_2\text{-P}(\text{SiMe}_3)_2][\mu_3\text{-P}(\text{SiMe}_3)_2](\text{THF})\}_2$ (**III**). These compounds are nevertheless isostructural and similar to $\{\text{Li}_2[\mu_2\text{-P}(\text{tBu})_2][\mu_3\text{-P}(\text{tBu})_2](\text{THF})\}_2$ (**IV**).¹⁰ All three compounds lie on crystallographic inversion centers and contain a core ladder structure consisting of four antiparallel E-Li (E = As, P) steps. Compound **I** is not only the first structurally characterized

lithium arsenide exhibiting this type of skeletal structure but also it is the first containing five-coordinate arsenic. As-Li bond distances in **I** vary significantly with the mean of 2.63 Å for those associated with the five-coordinate As [As(1)-Li(1) = 2.63(2) Å, As(1)-Li(2) = 2.69(2) Å, As(1)-Li(2') = 2.57(2) Å] being longer than that of 2.53 Å for those involving the four-coordinate As [As(2)-Li(1) = 2.51(2) Å, As(2)-Li(2) = 2.54(2) Å]. The difference of 0.10 Å between these means is similar to those of 0.12 Å and 0.13 Å for the corresponding means in **III** and **IV**, respectively. The central ring is required crystallographically to be exactly planar and, with endocyclic torsion angles of only $\pm 8^\circ$ in the Li(1)-As(1)-Li(2)-As(2) rings, the Li₄As₄ framework is overall fairly flat (max. deviation = 0.107 Å, mean deviation = 0.090 Å from the least-squares plane). Endocyclic bond angles at the Li atoms [71.1(5)°, 72.7(6)°, 77.2(6)°] are consistently much larger than those at the As centers [108.9(6)°, 103.2(5)°, 105.8(7)°], and consequently the four-membered rings are skewed significantly from a square geometry. In accord with the situation in **III** and **IV**, the bonding arrangement at the three-coordinate Li atom in **I** is planar. The THF oxygen atom lies close to the least-squares plane through the [LiAs]₄ core (Δ = 0.3 Å), and the Li-O distance of 1.87(2) Å in **I** is similar to those of 1.89(3) Å in **III** and 1.92(1) Å in **IV**.

The negligible solubility of LiAs(SiMe₃)₂ in non-etherial solvents and its decomposition upon sublimation prevented the successful crystallization of this material. However, crystals of **II** could be grown from a pentane/THF solution of ether-free LiAs(SiMe₃)₂. These crystals readily lose THF to become a white powder. Sealing crystals inside thin-walled glass capillaries previously moistened internally with a pentane/THF solution stabilized the crystals for X-ray data collection. An ORTEP diagram showing the solid-state structure of **II** is presented in Figure 2. Table 4 lists the non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters while selected bond distances and angles are presented in Table 5.

Dimer **II** is isomorphous with its phosphorus analogue [(Me₃Si)₂PLi(THF)₂]₂. These compounds lie on crystallographic centers of symmetry and consequently their (E-Li)₂ rings (E = As, P) are strictly planar. The coordination geometry at Li and pnictogen is distorted tetrahedral. The only other dimeric lithium arsenides for which the solid-state structures have been determined

are $[(\text{Et}_2\text{O})_2\text{LiAsPh}_2]_2$ (**V**)⁵ and $(\text{DME})\text{LiAs}(\text{SiMe}_3)_2]_2$ ($\text{DME} = 1,2\text{-dimethoxyethane}$) (**VI**),¹¹ both of which contain four-coordinate Li, and $\{(\text{THF})\text{Li}[\text{As}(\text{tBu})\text{As}(\text{tBu})_2]\}_2$ ⁷ (**VII**) wherein the Li is three-coordinate. Variations in intramolecular steric and electronic effects of the ligands in **II**, **V**, and **VI** are reflected in the ring geometries. The mean of the essentially equal As-Li bond distances $[2.70(1), 2.67(1) \text{ \AA}]$ at 2.69 \AA in **II** is close to that of 2.73 \AA in **V** but it is considerably longer than the As-Li distance of $2.59(2) \text{ \AA}$ in **VI**. On the other hand, the As-Li-As angle at $98.2(4)^\circ$ in **II** is essentially identical with that of $99(1)^\circ$ in **VI**, and both are much larger than the Li-As-Li angles of $82.8(3)^\circ$ and $81(1)^\circ$, respectively; thus, as in **I**, the rings are distorted from a regular square geometry. The presence of phenyl substituents at arsenic in **V** results in a much larger Li-As-Li angle $[90.3(4)^\circ]$ compared to those in **II** and **VI** and, with the mean Li-As-Li angle at $88.3(4)^\circ$, the ring is approximately square.

Acknowledgements

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Supplementary Material Available

Complete tables of anisotropic temperature factor parameters, interatomic distances and angles, hydrogen atom coordinates and isotropic thermal parameters, and a listing of observed and calculated structure amplitudes for **I** and **II** (43 pages) are available from R. L. Wells.

References

1. B.J. Wakefield, *The Chemistry of Organolithium Compounds* (Pergamon Press Ltd., Oxford, New York, 1974).
2. W.N. Setzer and P.Von R. Schleyer, *Adv. Organomet. Chem.* **24**, 353 (1985).
3. E. Hey, P.B. Hitchcock, M.F. Lappert and A.K. Rai, *J. Organomet. Chem.* **325**, 1 (1987).
4. E. Hey-Hawkins and E. Sattler, *J. Chem. Soc., Chem. Commun.* 775 (1992).
5. R.A. Bartlett, H.V. Rasika Dias, H. Hope, B.D. Murray, M.M. Olmstead and P.P. Power, *J. Am. Chem. Soc.* **108**, 6921 (1986).
6. R.A. Bartlett, M.M. Olmstead and P.P. Power, *Inorg. Chem.* **25**, 1243 (1986).
7. A.M. Arif, R.A. Jones and K.B. Kidd, *J. Chem. Soc., Chem. Commun.* 1440 (1986).
8. Von G. Becker, G. Gutekunst and H.J. Wessely, *Z. anorg. allg. Chem.* **462**, 113 (1980).
9. *International Tables for X-ray Crystallography*, vol. IV (The Kynoch Press, Birmingham, England, 1974).
10. R.A. Jones, A.L. Stuart and T.C. Wright, *J. Am. Chem. Soc.* **105**, 7459 (1983).
11. Von G. Becker, C. Witthauer, *Z. anorg. allg. Chem.* **492**, 28 (1982).

Captions to Figures.

Figure 1 ORTEP diagram showing the solid-state conformation of $\{\text{Li}_2[\mu_2\text{-As}(\text{SiMe}_3)_2][\mu_3\text{-As}(\text{SiMe}_3)_2](\text{THF})\}_2$ (I), with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted. Primed atoms are related to the unprimed atoms by a crystallographic center of symmetry.

Figure 2 ORTEP diagram showing the solid-state conformation of $[(\text{Me}_3\text{Si})_2\text{AsLi}(\text{THF})_2]_2$ (II), with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted. Primed atoms are related to the unprimed atoms by a crystallographic center of symmetry.

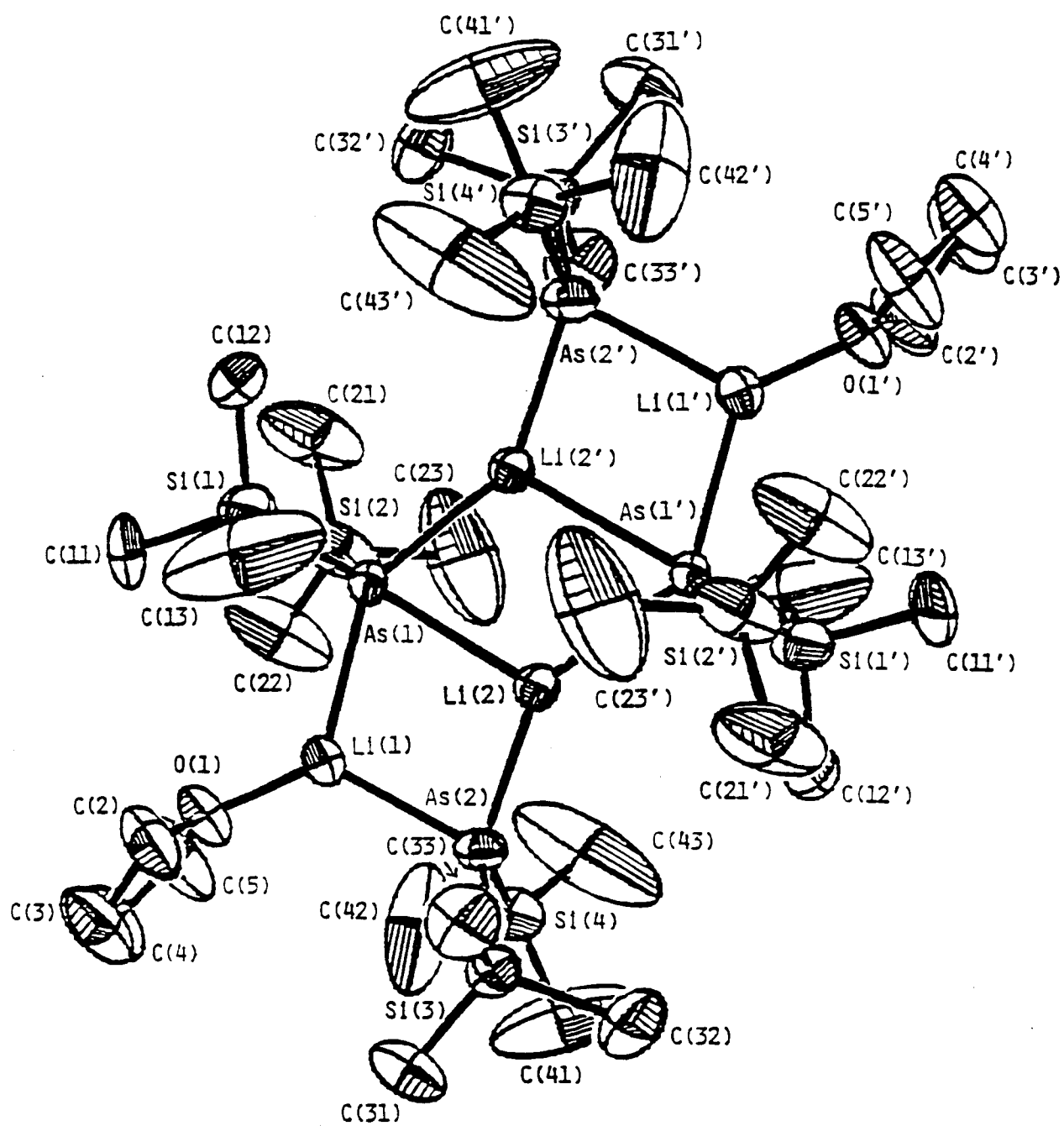


Figure 1

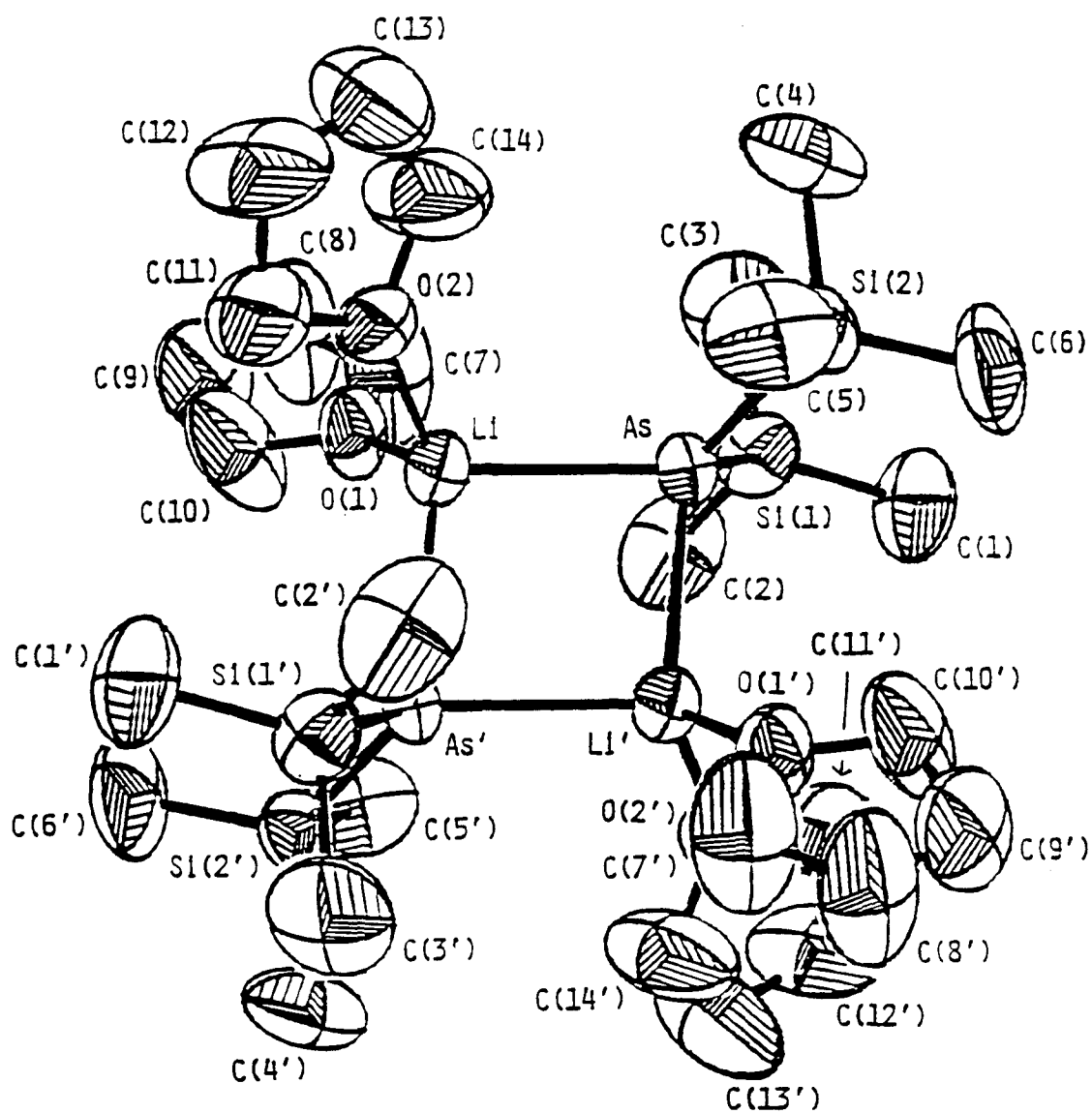


Figure 2

Table 1 Summary of crystallographic data and measurements for $\{\text{Li}_2[\mu_2\text{-As}(\text{SiMe}_3)_2][\mu_3\text{-As}(\text{SiMe}_3)_2](\text{THF})\}_2$ (I) and $[(\text{Me}_3\text{Si})_2\text{AsLi}(\text{THF})_2]_2$ (II).

	I	II
Molecular Formula	$\text{C}_{32}\text{H}_{88}\text{As}_4\text{Li}_4\text{O}_2\text{Si}_8$	$\text{C}_{28}\text{H}_{68}\text{As}_2\text{Li}_2\text{O}_4\text{Si}_4$
Formula weight	1057.20	744.92
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	10.147(1)	17.877(4)
b (Å)	19.665(2)	14.077(3)
c (Å)	16.768(2)	19.006(4)
β (°)	107.78(1)	109.16(2)
V (Å ³)	3186(1)	4518 (4)
Z	2	4
$D_{\text{calcd.}}$ (g cm ⁻³)	1.102	1.095
Radiation (wavelength)	Cu-K α (1.5418 Å)	Cu-K α (1.5418 Å)
μ (cm ⁻¹)	41.0	30.6
Temperature (°C)	25	25
Crystal dimensions (mm)	0.18 x 0.30 x 0.40	0.20 x 0.30 x 0.80
$T_{\text{max.}}:T_{\text{min.}}$ (relative)	1.00 : 0.60	1.00 : 0.72
Scan Type	ω -2 θ	ω -2 θ
Scanwidth (°)	$0.80 + 0.14\tan\theta$	$0.90 + 0.14\tan\theta$
$\theta_{\text{max.}}$ (°)	55	75
Intensity control refls.	3 4 2, 1 2 $\bar{2}$, 2 2 $\bar{3}$, 1 4 2	1 7 1, 2 2 $\bar{4}$, 3 3 1, 4 2 $\bar{2}$
Variation; repeat time (h)	<2% ; 2	<2% ; 2
No. of refls. (+ h , + k , $\pm l$) recorded	4071	4809
No. of non-equiv. refls. recorded	3906	4658
R_{merge} (on I)	0.035	0.039
No. of refls. retained [$I > 3.0\sigma(I)$]	1832	2463
No. of parameters refined	226	182
Extinction correction		$8(2) \times 10^{-7}$
R (R_w) ^a	0.053 (0.072)	0.060 (0.084)
Goodness-of-fit ^b	1.47	1.68
Max. shift: esd in final least-squares cycle	0.03	0.02
Final $\Delta\rho$ (e/Å ³) max.; min.	0.36 ; -0.28	0.53 ; -0.66

Table 1 (continued)

^a $R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$; $R_w = [\sum w(\|F_o\| - \|F_c\|)^2 / \sum w\|F_o\|^2]^{1/2}$; $\sum w\Delta^2$ [$w = 1/\sigma^2(\|F_o\|)$, $\Delta = (\|F_o\| - \|F_c\|)$] was minimized.

^b Goodness-of-fit = $[\sum w\Delta^2 / (N_{\text{observations}} - N_{\text{parameters}})]^{1/2}$.

Table 2 Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters^a for $\{\text{Li}_2[\mu_2\text{-As}(\text{SiMe}_3)_2][\mu_3\text{-As}(\text{SiMe}_3)_2](\text{THF})\}_2$ (I), with estimated standard deviations in parentheses.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
As(1)	0.1219(1)	0.09049(5)	0.03215(6)	6.91(3)
As(2)	0.1771(1)	-0.02175(7)	0.24577(6)	8.33(3)
Si(1)	0.2632(5)	0.1359(3)	-0.0374(3)	18.7(2)
Si(2)	-0.0089(5)	0.1766(2)	0.0595(3)	17.7(2)
Si(3)	0.3494(4)	-0.0993(2)	0.2973 (2)	9.3(1)
Si(4)	0.0753 (4)	-0.0061(2)	0.3494 (2)	10.7(1)
C(11)	0.3494(24)	0.2157(12)	0.0278(17)	48(1)
C(12)	0.1815(18)	0.1730(8)	-0.1392(8)	18(1)
C(13)	0.3890(21)	0.0817(22)	-0.0375(15)	56(2)
C(21)	-0.0842(25)	0.2302(11)	-0.0265(14)	31(1)
C(22)	0.0597(21)	0.2141(11)	0.1578(12)	28(1)
C(23)	-0.1793(24)	0.1344(19)	0.0694(24)	42(2)
C(31)	0.4829(16)	-0.0739(11)	0.3958(11)	18.4(7)
C(32)	0.2794(15)	-0.1856(7)	0.3151(9)	14.9(5)
C(33)	0.4365(15)	-0.1134(9)	0.2170(9)	15.6(5)
C(41)	0.1154(23)	-0.0605(16)	0.4330(10)	38(1)
C(42)	0.1197(24)	0.0683(12)	0.4035(11)	39(1)
C(43)	-0.0944(23)	-0.0058(24)	0.3131(15)	46(2)
O(1)	0.4232(8)	0.1308(5)	0.2514(5)	12.1(3)
C(2)	0.5521(15)	0.1236(11)	0.2517(10)	19(1)
C(3)	0.6421(16)	0.1450(11)	0.3362(13)	22(1)
C(4)	0.5541(17)	0.1777(11)	0.3726(11)	19(1)
C(5)	0.4221(17)	0.1655(10)	0.3185(11)	22(1)
Li(1)	0.2711(20)	0.0796(11)	0.1901(12)	9.3(6)
Li(2)	0.0520(18)	-0.0274(8)	0.0895(10)	7.4(4)

$$^a B_{\text{eq}} = (4/3)(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha)$$

Table 3 Selected bond distances (Å) and angles (°) for $\{\text{Li}_2[\mu_2\text{-As}(\text{SiMe}_3)_2][\mu_3\text{-As}(\text{SiMe}_3)_2](\text{THF})\}_2$ (I), with estimated standard deviations in parentheses.

<i>Bond distances</i>			
As(1)-Si(1)	2.288(6)	As(2)-Si(3)	2.282(4)
As(1)-Si(2)	2.283(5)	As(2)-Si(4)	2.297(4)
As(1)-Li(1)	2.63(2)	As(2)-Li(1)	2.51(2)
As(1)-Li(2)	2.69(2)	As(2)-Li(2)	2.54(2)
As(1)-Li(2')	2.57(2)	Li(1)-O(1)	1.87(2)
<i>Bond angles</i>			
Si(1)-As(1)-Si(2)	107.8(2)	Si(2)-As(1)-Li(2)	109.6(4)
Si(1)-As(1)-Li(1)	106.7(5)	Si(2)-As(1)-Li(2')	102.5(4)
Si(1)-As(1)-Li(2)	142.6(4)	Li(1)-As(1)-Li(2)	72.7(6)
Si(1)-As(1)-Li(2')	99.7(5)	Li(1)-As(1)-Li(2')	143.6(6)
Si(2)-As(1)-Li(1)	92.8(5)	Li(2)-As(1)-Li(2')	71.1(5)
Si(3)-As(2)-Si(4)	105.8(1)	Si(4)-As(2)-Li(1)	119.0(5)
Si(3)-As(2)-Li(1)	109.7(5)	Si(4)-As(2)-Li(2)	126.0(5)
Si(3)-As(2)-Li(2)	116.4(4)	Li(1)-As(2)-Li(2)	77.2(6)
As(1)-Li(1)-As(2)	105.8(7)	As(1)-Li(2)-As(2)	103.2(5)
As(1)-Li(1)-O(1)	130(1)	As(1)-Li(2)-As(1')	108.9(6)
As(2)-Li(1)-O(1)	125(1)	As(2)-Li(2)-As(1')	147.6(8)

Table 4 Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters^a for [(Me₃Si)₂AsLi(THF)₂]₂ (II), with estimated standard deviations in parentheses.

Atom	x	y	z	B _{eq} (Å ²)
As	0.27092(3)	0.10831(4)	0.01214(3)	6.94(1)
Si(1)	0.3390(1)	0.0273(2)	0.1181(1)	10.20(6)
Si(2)	0.2426(1)	-0.0072(2)	-0.0772(1)	9.90(5)
O(1)	0.1346(3)	0.2331(3)	0.1076(2)	11.3(1)
O(2)	0.0546(3)	0.2029(4)	-0.0562(3)	11.4(2)
C(1)	0.4337(6)	-0.0251(8)	0.1164(6)	16.0(4)
C(2)	0.3689(8)	0.1089(11)	0.1984(6)	19.4(5)
C(3)	0.2788(8)	-0.0650(8)	0.1431(6)	18.5(4)
C(4)	0.1755(7)	-0.1058(7)	-0.0651(6)	17.0(4)
C(5)	0.1901(7)	0.0536(9)	-0.1666(4)	15.8(4)
C(6)	0.3290(7)	-0.0678(7)	-0.0907(6)	18.8(3)
C(7)	0.1423(8)	0.1628(9)	0.1590(6)	23.6(4)
C(8)	0.0924(7)	0.1787(8)	0.2002(5)	21.9(3)
C(9)	0.0612(6)	0.2605(8)	0.1806(5)	19.3(4)
C(10)	0.0939(6)	0.2999(7)	0.1314(5)	21.9(3)
C(11)	-0.0084(7)	0.2648(7)	-0.0915(10)	18.6(6)
C(12)	-0.0724(7)	0.1963(9)	-0.1352(8)	20.9(5)
C(13)	-0.0487(9)	0.1027(9)	-0.1268(10)	27.8(8)
C(14)	0.0259(8)	0.1071(8)	-0.0660(11)	23.4(7)
Li	0.1583(6)	0.2350(7)	0.0138(6)	8.0(2)

$$^a B_{eq} = (4/3)(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha)$$

Table 5 Selected bond distances (Å) and angles (°) for [(Me₃Si)₂AsLi(THF)₂]₂ (**II**), with estimated standard deviations in parentheses.

<i>Bond distances</i>			
As-Si(1)	2.287(2)	As-Li'	2.67(1)
As-Si(2)	2.285(2)	Li-O(1)	1.96(1)
As-Li	2.70(1)	Li-O(2)	1.95(1)
<i>Bond angles</i>			
Si(1)-As-Si(2)	102.9(1)	As-Li-As'	98.2(4)
Si(1)-As-Li	120.2(3)	As-Li-O(1)	112.7(4)
Si(1)-As-Li'	115.3(2)	As-Li-O(2)	112.7(5)
Si(2)-As-Li	119.7(2)	As'-Li-O(1)	115.8(5)
Si(2)-As-Li'	117.0(3)	As'-Li-O(2)	117.9(5)
Li-As-Li'	81.8(3)	O(1)-Li-O(2)	100.2(6)

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